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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : H01L 23/488, H01B 1/06, B05D 5/12, B32B 27/38, 15/08, C08G 59/68, 59/40

A1

(11) International Publication Number: WO 97/07542

(43) International Publication Date: 27 February 1997 (27.02.97)

(21) International Application Number: PCT/US96/12761

(22) International Filing Date: 9 August 1996 (09.08.96)

(30) Priority Data:

08/514,049	11 August 1995 (11.08.95)	US
08/644,911	28 May 1996 (28.05.96)	US

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(81) Designated States: JP, KR, SG, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published

With international search report.

(54) Title: EPOXY RESIN BASED SOLDER PASTE

(57) Abstract

A method of making low and high mass assemblies at surface mount profile conditions utilizing a solder paste have a binder comprised of a thermosetting resin and cross-linking agent that also acts as a flux is described. The method of selecting the components and specific binders, including binders with a catalyst such as tin octoate are also described. The binder utilized has a gel point that is at or above the melting point of the solder powder and most preferably above such melting point.

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EPOXY RESIN BASED SOLDER PASTE

BACKGROUND OF THE INVENTION

This application is a continuation-in-part of Application Serial No. 08/514,049, filed August 11, 1995, the disclosure of which is incorporated herein by reference thereto.

Field of the Invention

The present invention relates to solder pastes and methods of soldering therewith.

The Prior Art

Solder paste (also called cream solder) is a paste-like, uniform mixture of a powdered solder and a pasty flux that can be used to solder many elements simultaneously by employing an atmosphere-heating means such as a reflow furnace. Due to these characteristics, solder paste has contributed to advance in surface mounting techniques for the manufacture of printed circuit boards.

Soldering with a solder paste is performed, for example, by applying the solder paste to the areas to be soldered on the surface of a circuit board by printing using a stencil and a squeegee. One or more electronic elements to be mounted on the surface of the circuit board, such as IC modules, chip capacitors, chip resistors, or the like are then placed on the printed solder paste and temporarily secured in place by the adhesive power of the solder paste. Subsequently, the solder is heated to melt in a heating apparatus such as a reflow furnace, thereby soldering the electronic elements to the circuit board to form an electronic device.

Solder paste, which has conventionally been used, consists of about 85%-92% of a powdered solder and about 8%-15% of a flux (also referred to as binder) on a weight basis. The flux typically is comprised of the following ingredients:

50%-70% by weight of a rosin or its derivative,
2%-7% by weight of a thixotropic agent,
0.1%-5% by weight of an activating agent, and
30%-45% by weight of a solvent.

Rosin or rosin derivatives are the main fluxing agents of the flux.

The powdered solders utilized in solder paste vary based on applications and target reflow temperatures. Shape and size of the powder is not critical, again being selected based on the application to which the solder paste will be put. For example, in surface mounting with a narrow pitch distance between adjacent leads, spherical powdered solder particles of about 250 to 400 mesh are preferred to prevent bridging between electrical leads.

Solder pastes described in the prior art include solder powders comprised of Sn, Pb, Bi, Cd, Zn, In, Sb, Ag, Cu and eutectic alloys of tin and lead, tin and bismuth (where a lead free alloy is called for) and tin, lead and silver.

Most solders are alloys of tin and lead. Pure lead melts at 327° C and pure tin melts at 232° C. When these two metals are alloyed, the alloy has a lower melting point than either of the individual components. Depending upon the percentage composition of the tin and lead, the melting point will vary. However, there is one alloy having a composition of 63% tin and 37% lead, known as the eutectic composition, that has the lowest melting point (183° C) of any of the possible mixtures. This eutectic composition has the characteristics of having a sharp and distinct melting point precisely at this temperature. That is, the solder alloy undergoes a phase change from solid to liquid at this point. All other compositions of tin and lead, other than the eutectic, are mixtures which do not melt sharply at any one temperature, but which pass through an intermediate range of plasticity in cooling from the liquid to the solid state.

Because many solder alloys exhibit a melting range rather than a pure melting point, a great deal of confusion exists over exactly what point may be considered to be the melting point of solder. For purposes of this invention, the melting point of a solder is considered to be that point at which the alloy transitions from a solid either to a liquid or to a plastic type composition, that is the melting point may be considered to be equivalent to the lower end of the melting range, or the solidus point.

The solder alloy in the solder paste is in the form of

finely divided particles (such as spheres or irregularly shaped particles), which in accordance with the present invention have a size distribution of from about 20 to about 45 microns, and preferably from about 20 to about 35 microns. These particles are frequently referred to as "solder powder." The powder is typically suspended in a binder matrix of a vehicle and a fluxing agent, to aid in the printing and reflow processes.

The use of synthetic thermosetting polymer resins together with soldering flux agents is described in U.S. Patent 3,791,027, granted February 12, 1974. Therein epoxide resin compositions are described wherein fluxing agents react with the epoxide resin to strengthen solder joints.

Electrically conductive adhesive compositions in which solder powder, a chemically protected cross-linking agent with fluxing properties and a reactive monomer or polymer (inclusive of epoxy resins) are described in U.S. Patent 5,376,403, granted December 27, 1994.

Polymers or oligomers which have carboxyl groups and act as both flux and hardener have been described in the recent art, in U.S. Patent 5,439,164, granted August 8, 1995. The patent describes a diffusion joining method used for Cu or Cu alloy contacting surfaces particularly adapted for preparing multilayer printed wiring boards.

Various soldering methods for electrically interconnecting/connecting components have been and continue to be in use. Surface mounting, using solder paste, facilitates soldering of electronic elements (components) together with increased accuracy and in a more simplified manner.

Reflow soldering profiles for various solder paste applications are described in the art, with the solder paste selected typically chosen based on temperature constraints of the elements and/or substrates involved. In this regard, see, e.g. U.S. Patent 5,250,843, wherein a method of reflow soldering is described utilizing infrared (IR) heating. In the method of such patent, the solder paste chosen for a preferred embodiment is ALPHA WS-601 solder paste, manufactured by Alphametals of Jersey City, N.J. This

preferred paste is a 90% metal material having a viscosity around 900 kcps.

The solder composition in the paste is a 63:37 eutectic alloy of tin:lead formed in spherical particles having diameters no larger than 45 microns due to the smaller openings in the stencil that are required for the method of the therein described invention. Such solder has a reflow temperature in the range of 183° C. Another solder paste described in the patent is a 90% metal composition having 700 kcps viscosity, with the solder composition in the paste being a 63:35:2 eutectic alloy of tin:lead:silver formed in spherical particles having diameters no larger than 45 microns. Such solder has a reflow temperature in the range of 183°C.

As noted by patentee, the described low temperature solder compositions have the advantage of being used with a wide variety of electrical components because reflow of such compositions induces less thermal stress on electrical components, so more standard components are capable of withstanding the reflow process.

As noted by reference to "MANUFACTURING TECHNIQUES FOR SURFACE MOUNTED ASSEMBLIES," Wassink, R.K. and Verguld, M.F., 1995 ELECTROCHEMICAL PUBLICATIONS, LTD., soldering methods (and equipment) have converged from various IR soldering concepts to one main method, namely, hot-convection soldering. Besides this method other methods are used, but only in specific cases, such as resistance soldering for outer lead bonding of TAB and for soldering on foils.

In Wassink et al., at pages 275, 276, a typical profile for reflow soldering is described. A hot-air convection soldering oven having a number of zones whose temperature can be controlled separately is used in order to attain the desired temperature profile along the length of the entire oven. Such profile enables all joint areas to reach the soldering temperatures with limited temperature differences between the joint areas of components with different thermal mass.

Wassink et al. describes the typical three step heating approach of the prior art frequently used in reflow soldering

using multiple hot-air convection ovens.

As also described in Wassink et al., the three steps are:

(i) starting with rapid heating to bring heat into the product (this reduces the length of the oven);

(ii) second step concerns temperature equalizing, i.e., to reduce the temperature differentials; usually a kind of temperature plateau for the hottest parts is pursued while the temperature rise of the coldest parts is chosen to be relatively slow; the effectiveness of this step can easily be assessed by the temperature differentials that exist on the assembly just before it enters the next step;

(iii) final rapid heating and subsequent cooling.

As further described in Wassink et al., each limit of the profile is determined by the maximum allowable thermal load of one of the parts of the assembly to be soldered.

- The maximum (peak) temperature is determined by the base material of the printed board. Higher temperatures than 280° C will cause delamination. (Note: In most cases the printed board is the hottest component.)
- The minimum soldering (peak) temperature is determined by the wetting of component metallizations.
- The maximum time and temperature of the equalize region is determined by the solder paste. In the case of too heavy a thermal treatment, the activator (flux) in the solder paste will be consumed already at this stage of the process.
- The time for which the solder is in the molten stage (in combination with a maximum temperature) is restricted by the formation of intermetallic layers inside the soldering joint. These layers make the soldered joint more brittle.

The specific values of the mentioned boundaries are determined based on the components and board material used.

A surface mount reflow profile for a 63 Sn/37 Pb solder illustrating the typical ranges is shown in Fig. 1.

In Patent U.S. 3,791,027 ("Angelo"), the disclosure of which is incorporated herein by reference thereto, polymers and other materials which contain chemical functionalities; such as, amide, amino, carboxyl, imino, and mercaptan; which serve as flux agents are described. When soldering metals, these materials can be combined with materials which contain other functionalities; such as, epoxide and isocyanate to produce thermosetting polymers. Angelo describes three polymer categories in his invention which are set forth below.

1. Chemical functionalities; such as, carboxy terminated polybutadiene and carboxy terminated polyisobutylene, which, when used alone, do not harden and are easily removed with solvents. These are in essence fluxes which contain the same chemical functionalities found in traditional soldering fluxes.

2. Formulations that are non-crosslinking and can be softened or melted with the addition of heat. Examples cited in Angelo include Versarid 712 and Acryloidat 70. Since cross-linking does not take place, these formulations are similar to standard rosin or resin based fluxes frequently used in reflow soldering which contain chemical functionalities such as amino, carboxyl, amide, etc. Thus the same chemical functionalities are present both traditional rosin and resin fluxes and in the examples cited in Angelo which do not chemically cross-link to form thermoset polymer and hence may be removed by using a solvent or may be reheated and remelted to enable resoldering of solder joints.

3. Combinations of materials, which contain the chemical functionalities necessary to promote solder wetting; such as, carboxyl, amino, etc., and materials that react chemically to form thermosetting polymers that cannot be easily removed through use of a solvent or reheated and remelted. Specifically Angelo shows examples of combinations of materials, which contain such functionalities, with epoxy resin materials which, when heated, form cross-linked

networks which are not easily removable or cannot be remelted. Angelo cites the usefulness of such combinations to reside in their ability to reinforce the strength of the solder joint in situations when there is a low probability that a solder joint will need to be resoldered.

Pennisi, et al., U. S. Patent 5,128,746, also describes the use of combinations of materials which contain chemical functionalities known to serve as fluxes and materials; such as, epoxy resins, which when reacted with the addition of heat, form chemically cross-linked polymers which add strength to solder joints and are not easily removable. Although Pennisi describes the function of the epoxy thermoset polymers as providing environmental protection to the flip-chip, the epoxy encapsulant described by Pennisi is also known to strengthen the fragile solder joints. Pennisi lists flux agents; such as, malic acid and other dicarboxylic acids that remove metal oxides and promote solder wetting. In essence, a material, malic acid, containing the carboxyl functional group, which is known to promote solder wetting, is combined with materials, epoxy resins, that form cross-linking, thermoset polymers.

In a third example, described in Capote, US 5,376,403, a material containing a chemical functionality, such as carboxyl, known to assist in solder wetting, is combined with materials that form cross-linking thermoset polymers that are used in ink systems that assist in the fusing of low melting alloy powders with high melting metals and assist in the adhesion of the resultant metal network to a substrate.

In each case (Angelo, Pennisi, Capote) in which a material containing a chemical functionality, known to promote solder wetting, is combined with materials such as epoxy resins that form thermoset polymers, a method of heating is described in which the assembly is heated rapidly above the solder melt point. The application of temperatures above the solder melt point 183°C is critical as the solder must liquify in order to wet the surface metal.

As thermosetting polymers are initiated by the application of heat in order to stimulate cross-linking reactions, it becomes necessary to understand the cure

kinetics involved in the curing of the material combinations selected. By chemically protecting the cross-linking material of the combination, Capote ensures that the cross-linking reactions are delayed and appropriate during the rapid heating process described in his invention.

Similar heating methods are described in Angelo and Pennisi, who both describe the application of heat during the soldering process as quick and rapid. As described previously in Wassink et al., a three step heating profile is typically used to solder electronic components to substrate boards. Rapid heating, as called for in Angelo, Pennisi and Capote, would adversely affect the parts and assemblies during soldering. This includes damage to components at high thermal excursion rates.

Thus, one frequently finds the heating step to be done using multizone ovens which allow materials in assemblies to achieve thermal equilibrium at temperatures above room temperature but lower than the solder melt point (183°C) in order to reduce thermal shock and subsequent damage. In SMT, this heating process in known as a surface mount reflow profile.

Therefore, in using combinations, as set forth by Angelo, Pennisi and Capote, in which materials containing chemical functionalities; such as carboxyl and amino, known to promote solder wetting, are combined with materials that form cross-linked thermoset polymers through the addition of the heat, heating processes are used that do not involve a rapid heating rate to the solder temperature but instead allow materials to be used in the final assembly to reach a thermal equilibrium, above room temperature but lower than soldering temperature. It becomes critical to understand the cure kinetics of the combination of thermosetting materials, in view of the desired non-rapid heating profile in order to prevent significant crosslinking of the combination prior to solder melt point.

The Present Invention

The present invention involves the use of compositions which function as flux and hardener for thermosetting resins and in particular epoxide resins, the resins of choice,in

solder paste formulations which find application in and are adopted for use in electrically connecting metal bond sites of a first electrical component to a metal bond site of a second electrical substrate to provide a thermoset polymer residue encased electrical solder connection under conditions corresponding to the appropriate surface mount reflow soldering profile for the architecture and composition of components and bond sites. The solder paste compositions of the present invention are formulated based on reflow temperature profile and the solder powder component selected for use in such solder pastes.

Thus, in accordance with the present invention, the soldering profile in such instances includes heating the assembly components to a temperature below the soldering temperature to prevent damage to the assembly parts that are susceptible to injury at high thermal excursion rates. This heating step is dependent on the size, mass and materials used in the assemblies and is referred to in the art as the soak or equilibrium stage of the profile. In connection with computer mother boards, telecommunications equipment and panels of smaller assemblies, the target temperature at the end of the soak step preferably approaches the melt point of the solder and may range from about 20°C below to the melt point of the solder powder in the paste up to the melt point thereof. The period of application of heat to achieve the target equilibrium temperature typically varies and may be from about 30 to about 120 seconds for large surface mount assemblies. The soaking step is preceded by a rapid increase in temperature, called the ramp step; the rate of increase in temperatures is selected to achieve maximum heat input without injury such as microcracks, warping and the like and is dependent on the involved architecture and materials. In the case of typical large surface mount assembly temperature increases of about 1°C to about 4°C per second prior to soak are the norm. The final step involves a rapid heating step following soak where the assembly is quickly heated to a temperature above the solder powder melting point in order to form the metal interconnection between the assembly components. Typically one component of the assembly is an

electrical component such as a packaged or unpackaged integrated circuit and the other component is a substrate for microelectronic circuitry on which the metal bond sites are located. In the art this step is referred to as the spike stage with a total time above melt point typically ranging from about 30 to 90 seconds. The peak temperature at any locus on the assembly is preferably in the 205°C to 235°C range.

For low thermal mass assemblies; that is, assemblies less than .062 inches thick and/or assemblies having an area typically 10 square inches or less, heat input is typically achieved using a smooth non-stepped ramp at the rate of 1°-4°C per second. Solder melt typically is achieved for low thermal mass assemblies in a time frame varying from something less than a minute up to about three minutes.

As the thermal mass of the assembly increases, slower heating rates and stepped processes are employed to bring such assemblies up to thermal equilibrium prior to reflow.

A criteria for selection and combination of thermosetting resin and cross-linking agent (whether in the presence of catalyst or otherwise) in order to achieve the requisite sequence of achieving solder melt before the gel point is reached resides in selecting a thermosetting resin and cross-linking agent combination that when heated using differential scanning calorimetry ("DSC") displays initiation of exothermic reaction with the range of about 140° C to 180°C for lead tin eutectic mixture. Exothermic activity as observed using DSC correlates to cross-linking activity. The peak of said exotherm in turn correlates with the level of cross-linking that indicates gel formation.

Although in the final analysis gel formation for the specific combination is determined empirically and exceptions occur, the criteria for selection that is generally applicable is to choose polymer systems wherein exothermic activity, as observed using DSC, is preferably initiated at a temperature no lower than 40°C below the solder melting point and where the peak exothermic activity registered occurs at a temperature above the solder melting point.

Anhydrides, including, in particular, highly active polyanhydrides, are the preferred dual-functioning cross-linking and flux agents for the epoxy resin solder paste of the present invention.

Also, in accordance with the present invention, the solder paste can be formulated to provide a solder joint which can be probed after reflow soldering in order to evaluate the integrity of the solder joint (electrical connection).

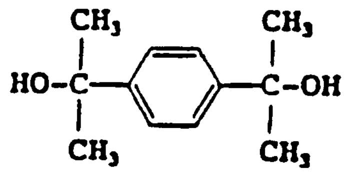
In addition to the aforesaid anhydrides, other cross-linking agents that are suitable for use in the present invention, though not necessarily with the same order of success, include materials containing chemical functionalities, such as carboxyl, amino, imino, amide, and mercaptan, as described in Angelo, that inherently act as fluxing agents as well as cross-linking agents. These materials are then selected to possess the critical attribute of delaying the occurrence of polymerization so that the resin gel point is reached after solder melt.

Amine cross-linking agents that provide the requisite latency (gel point formation at or above the melting point of the solder powder), such as Aificure --LX-1 (manufactured by Ajinomoto Co., Inc., Tokyo, Japan), which is heterocyclic diamine having an active hydrogen equivalent 67, may be used.

Amides and other known nitrogen containing curing agents such as melamine, dicyandiamide, imidazoles, hydrazides, thioureas and the like may also be used as cross-linking agents.

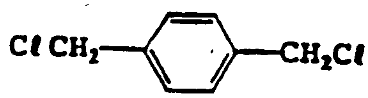
Also useful as crosslinking agents are the well-known polydric phenols which are polycondensates of one or more phenols such as phenol, various alkylphenols and naphthols with aldehydes such as formaldehyde, acetaldehyde, acrolein, glyoxal, benzaldehyde, naphthaldehyde and hydroxybenzaldehyde or ketones such as cyclohexanone and acetophenone, vinyl polymerization type polyhydric phenols such as polyvinylphenol and polyisopropenylphenols, the polyhydric phenols of the present first invention, Friedel-Crafts type reaction products of phenols with diols such as those

represented by the formula (1):



Dialkoxy compounds represented by the following formula (2):

or, dihalogens represented by the following formula (3):



and Friedel-Crafts type reaction products of phenols with diolefins such as dicyclopentadiene and diisopropenylbenzene.

In assemblies where the inherent fluxing ability of the cross-linking agent is insufficient to form proper metallurgical solder connections, it may be necessary to add additional fluxing agents in order to increase the flux activity to the formulation.

Where the cross-linking agent, in the amounts used, has inadequate activity as flux to achieve the required level of oxide removal, then added fluxing agent may be required.

The preferred additive is one that cross-links or binds chemically into the polymer matrix and does not retard the physical properties of the resultant polymer network. For this purpose carboxyl terminated polyester has been found to be a suitable flux additive.

In accordance with the present invention, a thermosetting binder resin for the solder powder constituent is combined with a cross-linking agent, preferably one that also acts as a solder flux and in the composition affects cross-linking of the binder resin at a temperature that does not inhibit soldering during surface mount reflow profile conditions.

In accordance with the present invention, an epoxy binder resin for the solder powder constituent is combined with a cross-linking agent that acts as a solder flux and a catalyst that activates cross-linking of the binder resin at

a temperature that does not inhibit soldering during surface mount reflow profile conditions.

SUMMARY OF THE INVENTION

The present invention relates to solder pastes suitable for use at surface mount reflow profile conditions and a method of electrically connecting an electrical component having a plurality of metal bond site terminations to a component carrying substrate having a plurality of metal attachments sites corresponding to the terminations of said electrical component, at surface mount reflow profile conditions. The solder paste utilized is comprised of (1) a solder powder having a solder melt temperature with a particle size distribution of from about 20 to about 45 microns and present in an amount, based on total weight of the solder paste, of about 65% by weight to about 95% by weight; and (2) a binder comprised of a thermosetting resin and a cross-linking agent that acts, below the solder melt temperature, as a fluxing agent which removes oxide coatings from the surface of the metal bond sites on said electrical component and on said component carrying substrate and from the surface of said solder powder when heated to said solder melt temperature. The thermosetting resin and cross-linking agent combination has a gel point at or above said solder melt temperature, and preferably above the solder melt temperature, when used in surface mount reflow profiles. The method comprises the steps of: a)removing oxide coating from the surface of metal bond sites and said solder powder while said binder is in liquid form; b) melting the solder to electrically connect the electrical component which has the plurality of metal bond site terminations to the component carrying substrate which has the plurality of metal bond site terminations corresponding to the terminations of said electrical component while said binder is in liquid form and prior to said binder reaching its gel point; then c) forming a binder gel; that is, reaching the gel point. Thereafter the gel may be cured to form a binder residue which encapsulates the electrical solder connections thereby providing protection and enhancing the mechanical connection.

The amount by weight of solder powder, based on total

weight of the solder paste, is preferably above 85% by weight and the preferred upper level is 92% by weight,, all percentages by weight being relative to total weight of the rosin paste.

The thermosetting resin is preferably an epoxide. The preferred cross-linking agents are a polyanhydride and carboxy terminated polyesters.

Another aspect of the present invention relates to forming a flexible binder residue; then inserting a probe through said flexible binder residue into contact with said electrical connection to check the integrity of said connection; then, withdrawing probe; and then assuming confirmation of the integrity of the connection, optionally hardening said binder residue.

The present invention also relates to a method of producing a low thermal mass assembly by electrically connecting an electrical component having a plurality of metal bond site terminations to a component carrying substrate having a plurality of metal attachments sites corresponding to the terminations of said electrical component utilizing a solder paste comprised of (1) a solder powder having a solder melt temperature with a particle size distribution of from about 20 to about 45 microns and present in an amount, based on total weight of the solder paste, of about 65% by weight to about 95% by weight; and (2) a binder comprised of a thermosetting resin and a cross-linking agent that acts, below the solder melt temperature, as a fluxing agent which removes oxide coatings from the surface of the metal bond sites on said electrical component and on said component carrying substrate and from the surface of said solder powder when heated to said solder melt temperature. The thermosetting resin and cross-linking agent combination have a gel point at or above, and preferably above, said solder melt temperature, when used in surface mount reflow profiles. In this method the low thermal mass assembly is ramped at the rate of about 1oC to about 4°C per second for a time sufficient to achieve solder melt and electrical interconnection. The steps of the method occur sequentially during ramping, as follows:

1. oxide coating is removed from the surface of the metal bond sites and the solder powder while the binder is in liquid form;

2. the solder is melted to electrically connect the electrical component having a plurality of metal bond site terminations to the component carrying substrate having a plurality of metal attachment sites corresponding to the terminations of said electrical component (the binder is in liquid form during this step and solder melt occurs prior to the binder reaching its gel point); then

3. the binder gel is formed at the gel point. Thereafter, the resultant gel is cured to form a binder residue encapsulating said electrical solder connections.

The amount by weight of solder powder, based on total weight of the solder paste, is preferably above 85% by weight and the preferred upper range is 92% by weight.

The preferred thermosetting resin is an epoxide. The preferred cross-linking agents are polyanhydride and carboxy terminated polyesters.

Another aspect of the method applicable to low thermal mass assemblies relates to forming a flexible binder residue; then inserting a probe through said flexible binder residue into contact with said electrical connection to check the integrity of said connection; then, withdrawing said probe. The binder residue can then if desired be further cured to harden the binder residue.

Yet another aspect of the present invention relates to a solder paste for electrically connecting a metal bond site of a first electrical component to a metal bond site of a second electrical component and for forming a solder residue encased electrical solder connection between said first and second components at solder reflow conditions. The solder paste is comprised of from about 65% by weight to about 95% by weight based on total weight of solder paste of a solder powder having a solder melt temperature; an epoxy resin; a cross-linking agent for the resin that also acts as a fluxing agent that removes oxide coatings from the surface of the first and second electrical components and the solder powder below the solder melt temperature of said solder; and a catalyst for

catalyzing cross-linking of said epoxy resin with said cross-linking agent, the peak exotherm of said mixture of catalyst, epoxy resin, and cross-linking agent as measured using DSC at a ramp rate of 10° per minute being at or above the solder melting point whereby the gel point of said cross-linked epoxy resin is reached after solder melt. The preferred catalyst is tin octoate. The preferred cross-linking agents are polyanhydrides.

The solder paste may be formulated to provide a solder residue that is flexible, allowing a probe to pass through the solder residue and access the solder connection encased by said solder residue. The solder paste can include a non-reactive flexibilizer which imparts flexibility to the solder residue after reflow soldering. The flexibilizer may be reactive and contain epoxy functional sites that, after reflow soldering, are incorporated into the backbone of the cross-linked epoxy resin.

Another aspect of the present invention relates to a method for selecting the components of binder component of a solder paste useful in forming encapsulated electrical interconnections in accordance with a surface mount reflow profile wherein the binder is comprised of a thermosetting resin, a cross-linking agent that also acts as a flux and optionally a cross-linking catalyst which comprises: a) identifying the melting point of the solder powder component; b) heating the binder to a temperature exceeding the melting point of the solder; c) measuring the exothermic activity of the binder during heating step b); d) identifying the temperature at which peak endothermic activity occurs; and e) selecting as a binder for said solder paste a binder that displays peak exothermic activity at or above the melting point of the solder.

The selection method suitably also includes identification of the initiation of exothermic activity and selection of the binder also based on initiation of thermal reaction. The binder selected is one that wherein initiation of exothermic activity occurs at a temperature that is no lower than 40°C and preferably no lower than 30°C, below the solder melt temperature.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a surface mount reflow profile for 63 Sn/37 Pb solder illustrating typical parameters where such solder is used.

Fig. 2 is the specific profile referred to in Example 1.

Fig. 3 is a graphic representation charting heat change versus temperature of the binder described in Example 1.

Fig. 4 is a graphic representation charting heat change versus temperature of the binder described in Example 4.

DETAILED DESCRIPTION OF THE INVENTION

One embodiment of the invention relates to a solder paste, which includes a catalyst. The solder paste comprises (1) solder powder and what is commonly referred to in the art as a binder, which binder, in accordance with the present invention, comprises (2) thermosetting resin, preferably an epoxy resin, (3) a cross-linking agent for such resin, which also functions as a fluxing agent during reflow soldering, and (4) a catalyst. The components of the solder paste binder are selected and combined to form in combination a composition having a gel point at or above the soldering temperature whereby soldering is not inhibited by gelling prior to soldering when used in surface mount reflow profiles. As used herein, gel point is the state at which the composition will no longer flow and cannot be displaced by the molten solder. Simply stated, the process of the present invention will not produce a satisfactory electrical connection if, prior to solder melt, which occurs at the solder melt temperature, the gel point of the involved epoxy resin system is reached. The cross-linking agent acts as flux during the soldering step for the solder powder and for the contact areas electrically connected by the solder. The cross-linking agent cures the epoxy resin and performs this latter function paired with a catalyst that catalyzes cross-linking activity and causes gel formation at or above the soldering temperature. Other objects and advantages will become apparent to those skilled in the art from a review of the detailed description of the invention which follows.

In systems of the present invention, where electrical connections along a single axis are involved and surface

mount reflow soldering is effected by powdered solder melt in a liquid epoxy resin system, the sequencing of stages of cross-linking vis-a-vis reflow soldering is critical.

It is essential that the gel point of the system not be reached prior to formation of the connection by liquid solder (solder melt) which connection occurs at surface mount reflow solder temperature.

It has been observed that where the gel point is reached before melting of the solder, the solder does not wet and does not effectively engage the opposing loci to be electrically connected by the solder powder component of the solder flux because solder flow is restricted.

It is believed that the criticality of this requirement in the system of the present invention derives from the inability of the solder to flow in a resin system where the gel point has been reached. It is believed that where the resin system carrying/binding the solder powder and enveloping the solder melt produced therefrom is liquid, even where the viscosity is great, effective fluxing of the solder particles which form the melt occurs. In fact, where a mixed phase exists, wetting, bonding and fluxing occur; however, once the gel point is reached and melt formation occurs after the gel point is reached, observation of the cured product demonstrates that successful connection is not achieved. There is a failure of proper melt formation, wetting and flow.

One aspect of the present invention relates to the selection and use of an epoxy resin based binder for solder paste that finds utility in surface mounting following surface mount reflow profiles for specific applications. In one embodiment of the invention the binder is comprised of an acid anhydride epoxy resin system. The solder paste of the present invention is composed of powdered solder in a binder comprised of an epoxy resin, an anhydride cross-linking agent for the resin that also functions as a fluxing agent at reflow soldering conditions and a catalyst that, when paired with the cross-linking agent activates cross-linking and causes transformation of binding resin to a gel after solder melt. The combination of compounds comprising the solder

powder binder is selected to provide an epoxy based binder which does not reach gel point prior to solder melt and formation of an electrical connection by said solder melt at surface mount reflow soldering conditions.

Selection of Binder System Components for Given Reflow Profiles

As noted herein, the present invention relates to solder paste formulations and methods of their use specifically adopted for forming protectively encased isotropic electrical interconnections at reflow profile conditions used in the manufacture of small and large mass assemblies. Such reflow profile conditions require application of heat over time and binder formulation is critical to achieving satisfactory wetting and solder melt to provide electrical interconnection at the bond sites as well as satisfactory encasement/mechanical bonding.

In choosing the binder for the solder paste used in the present invention, selection of thermosetting resin and cross-linking agents having the dual functions required in the present invention is critical in order to enable satisfactory electrical and mechanical bonding at the electrical bond sites to take place. The binder requirements and selections are discussed below.

During the reflow profile, the polymer must not reach its gel point before peak soldering temperatures since the molten solder must displace the polymer in order to wet the bonding surface. If the polymer reaches its gel point too quickly, a polymer barrier is formed between the metal surfaces. Since this gelation inhibits the solder from wetting the substrate metal bond pad, it is critical to understand the curing mechanism and kinetics of the polymer in order to understand the effect on soldering.

In thermoset polymers, the addition of heat initiates the irreversible reaction between the epoxy resin and the cross-linking agent. During the cure process the epoxy resin molecules react with the cross-linking molecules to form long polymer chains and networks with increasing viscosity. As the network grows, a point of infinite viscosity is reached called the gel point. At this point the polymer changes from a

viscous liquid to a solid that does not flow.

The gel time of thermosetting resins is usually found under isothermal conditions. For example, epoxy samples can be heated at a set temperature and tested using viscosimetric methods to find the gel time. An example of such a method is to heat epoxy resins in sample pans while measuring resistance to flow.

Since the method of heat during the process described in this invention is not isothermal but rather involves a slow heating of the sample to soldering temperatures, it is important to instead estimate the gelation of the polymer by examining the cure kinetics.

Several techniques can be used to examine cure kinetics of the thermoset polymers. One such method is dynamic mechanical analysis (DMA), which measures the polymer's ability to store and dissipate mechanical energy. Another common technique is to use differential scanning calorimetry (DSC), which measures changes in heat.

As the chemical reaction of thermoset resins during polymerization is exothermic, this change in heat can be measured using DSC and related to the extent of chemical reaction. As described by Hadad in <u>Epoxy Resins, Chemistry and Technology</u>, May, ed., Marcel Dekker, 1988, p. 1130, "an assumption is made that the amount of energy given off during the cure is proportional to the extent of chemical reaction." Using techniques described by Hadad it is possible to estimate the kinetic activation energy required for initiation of polymerization. One such method involves generating DSC scans using different heating rates as described in ASTM Method E 698-79. However, since the critical gelation point in order to prevent proper soldering interference as described in this invention must be determined empirically, DSC will be shown to serve only as a guide for proper material combinations as the soldering process has previously been described as ranges. Therefore, a single DSC scan at a single heating rate is used to show the relationship between cure kinetics of thermosetting polymers and their applicability for use in the method of soldering described in this invention.

The following examples serve to illustrate a mode of

practicing the invention including selection of solder paste binder components.

EXAMPLE 1

A mixture of a bisphenol A epoxy resin (Shell Epon 828), methyl tetrahydrophthalic anhydride (MTHPA) (Lonza AC220J) and the catalyst Tris(dimethylaminomethyl)-phenol, commonly referred to as DMP-30 (Lonza AC-30) was prepared according to formulations as described in literature available from the chemical suppliers:

Epon 828	55 parts
MTHPA	43 parts
DMP-30	2 parts

The resultant composition was spread onto a copper heated to 250°C along with a slug of 63Sn/37Pb solder in accordance with the method set forth by Angelo (US 3,791,027) and in heated rapidly as described in Pennisi US 5,128,746 and Capote 5,376,403. It was observed that the anhydride (MTHPA) cleaned the surface oxides from the metal surfaces which allowed the solder to wet onto the copper and form a metallurgical interconnect.

This same mixture was then spread onto the metal surface of an FR-4 epoxy glass substrate plated with copper along with a slug of 63Sn/37Pb solder. The substrate, containing the epoxy composition and the solder slug, was placed into an IR reflow oven with multiple heating zones. The temperatures of the zones and the belt speed of the oven had previously been profiled to yield substrate surface temperature profile as shown in Fig. 2.

Using this temperature profile the solder slug did not wet the copper surface on the FR-4 and form a metallurgical connection. Instead the solder slug remained in its original shape and was encapsulated in the cured epoxy.

In addition to the empirical soldering tests described above, DSC was used to examine the cure kinetics of the above epoxy. Using a 50 mg sample and a heating rate of 10°C/min from 50°C to 230°C, the onset of the cure exotherm was observed at 100°C while the peak exotherm was observed at 130°C, as shown in Fig. 3. Therefore, using a heating rate of 10°C/min., the maximum exotherm of the cure reaction occurs 50°C below the

melting point of the solder.

EXAMPLE 2

Using the same resin and anhydride combination as in Example 1, Lonza ACPI (a proprietary imidazole) was used as a catalyst.

Epon 828	55 parts
MTHPA	43 parts
ACPI	2 parts

This mixtures was used with solder slugs heated rapidly on copper. The anhydride cleaned the metal oxides and the solder wet and spread onto the copper surface. When the composition was spread onto copper over FR-4 organic substrate and heated in the multiple zone heating oven, however, the result was the same as described in Example 1. The solder did not change shape and did not spread onto the metal surface.

The DSC scan from 50°C to 230°C at 10°C/min on a 50 mg sample showed the exotherm onset to begin at 100°C and peak at 130°C. Again, although rapidly heating the combination of materials allowed the solder to spread onto the copper, when heated slowly to solder melt point using a multiple zone oven the epoxy system described did not have the necessary latency to remain liquid before soldering.

Similar results were observed using the Epon 828 and MTHPA combination with several other known anhydride cured epoxy catalysts, including Dimethylaminomethylphenol (Lonza AC-10), zinc octoate (Shepard Chemicals), Benzyldimethylamine (Lonza BDMA), Diazabicycloundecene (Air Products Amicure DBU-E), 2-ethylhexanoic acid salt of Diazabicycloundecene (Air Products Amicure SA-102), 2-heptadecylimidazole (Air Products Curezol 2MA-OK), 2-Heptadecylimidazole (Air Products C17Z), 2,4-Diamino-6(2'methylimidazoleyl-(1'))ethyl-s-tri (Air Products 2MZ Azine).

In each case the catalyst was used with a bisphenol A resin (EEW 190) such as Shell Epon 828 and Methyl Tetrahydrophthalic anhydride at 80 parts based on the weight of the resin. Using the catalysts stated above at 1-5 parts based on the weight of the resin, the mixtures were found to clean the metal oxides and promote spreading of 63 Sn/37 Pb solder to

copper when heated rapidly, but cured too quickly and inhibited soldering when heated slowly in a multizone conveyorized heating oven as described in Example 1.

EXAMPLE 3

Stannous octoate (Ferro Bedford Catachek 860) was selected as a catalyst for the bisphenol A resin, MTHPA composition as described in example 1.

Epon 828	55 parts
MTHPA	43 parts
Stannous octoate	2 parts

This mixture was used with solder slugs heated rapidly on copper. The anhydride cleaned the metal oxides and the solder wet and spread onto the copper surface. When the composition was spread onto copper over FR-4 organic substrate and heated in the multiple zone heating oven, the solder spread onto the metal surface of the copper and the epoxy was partially gelled. Thus the catalyst selection with this combination of resin and crosslinking agent provided the latency for gelation to take place after soldering.

The DSC scan from 50°C to 230°C at 10°C/min on a 50 mg sample showed the exotherm onset to begin at 150°C and peaked well above 200°C, as shown in Fig. 4. Thus, the peak exotherm, which is used to predict latency, occurs well above the solder melt point of 183°C.

EXAMPLE 4

Using stannous octoate as a catalyst with MTHPA along with a multifunctional resin such as N,N,N',N'-Tetraglycidal -4,4'-methylenebisbenzenamine (Ciba Geigy MY720). This tetra-functional resin has a higher reactivity than one based on bis phenol A. A mixture of MY720 with MTHPA at 90% of the stoichiometric ratio was prepared with stannous octoate used as the catalyst and added at 1 part based on the weight of the resin.

MY 720	45
MTHPA	54
Stannous octoate	1

Using this composition in the rapid heating method described in Example 1 the solder spread and formed a metallurgical

connection to the copper. However, when using the heating method involving the multizone oven the solder did not spread or wet onto the copper. Eliminating the stannous octoate and using the MY70/MTHPA combination described showed the same result. The solder was inhibited from wetting the copper when heating the sample in the multizone oven.

When cycloaliphatic resins such as 3,4-Epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (Union Carbide ERL-4221) are used in combinations with MTHPA are used with stannous octoate as the catalyst the soldering result observed is similar to Example 1. The composition cures before solder melt point and inhibits the spread of the solder to the copper.

A DSC scan of the composition:

ERL-4221	49 parts
MTHPA	49 parts
Stannous Octoate	2 parts

at a heating rate of 10°C/min showed the exotherm onset at 90°C with a peak exotherm at 155°C. Thus, the exotherm peak, which correlates to the chemical reaction rate, is lower than the melting point of the solder alloy.

A blend of epoxy resins Epon 828 and ERL 4221 was used with MTHPA and stannous octoate as a catalyst.

ERL-4221	24.5
Epon 828	24.5
MTHPA	49
Stannous Octoate	2

This system solder soldered 63 Sn/37Pb alloy to copper when heated rapidly but did not solder using the multizone heating oven. The DSC onset temperature began at a higher temperature of 120° C compared to the composition using only the cycloaliphatic resin (ERL-4221). Although the peak exotherm was nearly identical in temperature to the single resin system yet the height of the exotherm was lower with the resin blend system indicating less heat given off and therefore less chemical activity. Thus, blends of highly reactive resins such as cycloaliphatic resins with MTHPA do not provide the necessary latency.

EXAMPLE 5

A blend of bis phenol A system, MTHPA and a dicyandiamide type catalyst (Ajinomoto Ajicure AH-150) was used at various catalyst levels.

Epon 828	52-56	parts
AH-150	40-43	parts
AH-150	1-8	parts

Using catalyst levels of 1-2 parts based on the weight of the resin were found to solder the 63 Sn/37 Pb alloy both using rapid heating as well as using the multizone oven. However, when used at concentrations above 3 parts based on the weight of the resin the compositions inhibited the solder from spreading using the multi-zone heating profile. Thus, the catalyst level is critical to the rate of reaction. DSC exotherms revealed that the onset of the peak exotherm occurs at lower temperatures as catalyst concentration increases.

The Reflow Profile

The cross-linking catalyst (accelerator) selection is based on the need to inhibit gelation during the soldering process. The most important embodiment of the present invention involves the soldering method known as reflow soldering, as used with solder paste. In reflow soldering, solder paste is screen printed, stencil printed or dispensed onto metal bond sites on a circuit board or substrate. The components to be soldered to the circuit board or substrate are then placed onto the solder paste. The PCB or substrate is passed through an oven containing different heating zones. Three zones are typical. The first zone, or heating stage, is commonly called the ramp. In this zone, the surface temperature of the board is quickly raised to heat the materials of the board and components. In the second zone, known as the soak, the temperature of the board is allowed to equalize at this temperature range for a period of time that may be of short duration (1-3 minutes) in order to reduce temperature differentials on the surface of the board and components. The soak time will depend on the type of board, solder and components used. The third step involves a quick temperature spike to exceed the solder melt point. Therefore, the solder melting temperature dictates the temperatures of the zones. Since melting point of 63 Sn/37 Pb is 183° C, the soak

temperature is generally 120-160° C. The peak temperature at reflow is generally 200-300° C.

It has been found that polyanhydrides; such as polysebasic polyanhydride (PSPA), polyadipic polyanhydride(PADA), polyazelaic polyanhydride (PAPA), have a greater flux activity compared to derivatives of phthalic anhydride, such as methyltetrahydrophthalic anhydride. Therefore, in accordance with the present invention, the use of aliphatic polyanhydrides are preferred as flux agents for solder paste compositions.

Catalyst

The selection of the catalyst is critical and is based on the ability of the catalyst in the epoxy system to catalyze the cross-linking to the point of gelation (gel point) during or after the reflow process, without inhibiting reflow soldering.

By way of explanation, an uncatalyzed combination of a bisphenol A resin combined with a phthalic anhydride derivative, such as MTHPA, when used in a reflow soldering process, would not inhibit soldering but would also not reach its gel point during the reflow process. Such systems would require 6-48 hours of post-cure below soldering temperature (typically 150°C) in order to reach gelation and fully cross-link. Therefore, a catalyst is necessary to reduce the overall time of cure of these systems. However, it has been observed that, if a catalyst is selected which is too active, the system will reach gelation below the soldering temperature and inhibit the soldering process by forming a physical barrier between solder and target metal.

Anhydride catalysts of the amine type have shown this detrimental phenomenon. Examples of unacceptable catalysts are benzyldimethylamine dimethylamino methyl phenol, tris (dimethylamino methyl) phenol, triethanolamine and monoethanolamine. When these amines are used as catalysts together with bisphenol A epoxy resins, such as shell EPON 828, and phthalicanhydride derivatives such as MTHPA using the standard reflow protocol, premature gelation results which inhibits proper soldering.

Other common anhydride-cured epoxy catalysts have been

shown to be detrimental to soldering, as detailed in Example 2, when using blends of bisphenol A resins and MTHPA.

Tin octoate, the catalyst of choice for these systems, is a metal salt of tin and 2-ethylhexoic acid. Although not wishing to be bound, it is believed that the activity of the catalyst arises from the oxidation of the tin from Sn^{+2} to Sn^{+4} and the dissociation of the tin from the 2-ethylhexoic acid. When tin octoate is tested using differential scanning calorimetry, an exotherm is observed at 185-190° C. Although not wishing to be bound, it has been observed and therefore it is believed that the temperature at which the exotherm occurs correlates to the temperature at which catalysis of cross-linking occurs. Accordingly, one method of evaluating onsets of catalytic activity where the mechanism of catalysis of the catalyst being evaluated corresponds to that of tin octoate is to correlate the exotherm of the catalyst with the temperature at which catalysis of cross-linking occurs.

In the present invention, the solder paste has a high content of solder powder and the soldering flux must clean both the metal oxides from the solder and the substrate metal. Compared to solder wire or bar, solder powder has a substantially higher level of solder metal oxides due to the increased surface area of the solder. Therefore, in solder paste, which contains solder powder, a higher flux activity level is required than in fluxes used in other solder mediums.

When used in combinations with PAPA and bisphenol A resins stannous octoate has been shown to effectively provide the required latency necessary to prevent premature gelation of polymer before soldering.

The following is an example of a solder paste of the present invention.

EXAMPLE 6

A combination of an epoxy resin, anhydride curing agent and a catalyst were combined in the following ratio

EPON 828	59 Parts
PAPA	39 Parts
Stannous Octoate	2 Parts

Which was combined with 63Sn/37Pb solder powder so that the

metal content of the composition was 90% by weight based on the total weight of the solder paste.

This composition was spread onto copper on FR-4 substrate and heated as detailed in Example 1. The polyanhydride cleaned the surface oxides of the metals allowing the solder powder to wet and spread onto the copper.

Another example of a suitable solder paste composed of solder powder and a binder, comprises a binder containing (1) an epoxy resin, diglycidal ether of bisphenol A with an epoxy equivalent weight of 185 - 192, (2) polyazelaic polyanhydride cross-linking and fluxing agent and (3) tin octoate catalyst and solder powder. The cross-linking agent is an anhydride cross-linking agent which also acts as fluxing agent. The PAPA cross-linking agent is paired with tin octoate catalyst that catalyzes cross-linking at a temperature at or above about the soldering temperature, thereby preventing premature gel formation prior to formation of the electrical connection(s) by reflow soldering.

The amount of catalyst in the composition preferably ranges from about 0.1 to about 5 weight % based on total weight of binder. In the case of tin octoate, the preferred amount is from about 1.5 to about 2.5 weight percent and the optimal amount is about 2.0 weight % based on the weight of the organic component of the solder paste.

<u>Flexibilizers</u>

It is an aspect of the present invention to provide a flexible solder paste thermosetting resin residue, inclusive specifically of epoxy residues that can be penetrated by a probe. Flexibility can be imparted to the cured epoxy resin structures of the present invention by adding flexibilizers which may be reactive or non-reactive.

Non-reactive flexibilizers include long-chain molecules that are not volatilized at reflow temperatures, do not contain epoxy functionality and remain unreacted after cure. Examples of non-reactive flexibilizers include cashew oil or esters of selected fatty acids. Since the flexibilizers chosen are not volatile under the temperature profile of reflow soldering conditions or subsequent cure, their function as flexibilizers in the solder residue encapsulating

the solder connection is maintained after reflow soldering. Thereafter, further cure below solder melt temperature, after a probe of the solder joint confirms achievement of satisfactory connection, can be used to obtain the degree of hardness required for the encapsulating residue.

Reactive flexibilizers contain epoxy functional sites which are incorporated into the backbone of the cured system. Examples of reactive flexibilizers suitable for use to impart flexibility to the solder paste epoxy residue of the present invention include glycidal ethers of aliphatic polyols, such as Heloxy Modifier 84 from Shell Chemicals or a dimer acid of diglycidal ester such as Heloxy Modifier 71 from Shell Chemicals. The long aliphatic chains of reactive stabilizers impart flexibility to the cured epoxy by lowering the cross-link density.

As noted by reference to Lee and Neville, Handbook of Epoxy Resins, 1967, McGraw-Hill, pp. 4-6, cross-link density refers to the number of cross-links per unit volume of material. Resins based on diglycidal ether of Bis A (DGEBA) are spaced by seven units, or seven aromatic rings. Other resins may contain 30-40 units between epoxy groups. The longer the spacing, i.e., the more groups between cross-link sites, the more flexible the cured epoxy.

The probe-ability, which corresponds to the flexibility of the cross-linked epoxy resin, can be adjusted by selection of the resin. Flexibility can be achieved by the use of aliphatic side groups as opposed to aromatic groups on the resin backbone, with advantage over bulky aromatic groups that tend to hinder motion and thus decrease flexibility more than aliphatic groups. The adjustment of flexibility by introducing substituents on the backbone of the epoxy resin decreases the number of cross-link sites per unit volume and the selection of such substituents is as matter of choice, easily verified by checking the probe-ability of the solder paste residue after solder melt at conditions replicating the reflow soldering profile. For example, carboxyl terminated butadiene-acrylonitrile (CTBN) elastomer can be incorporated into the backbone of the epoxy resins of the present invention and lower the cross-link density. Examples of CTBN

modifiers are HYCAR 1300X8 and HYCAR 1300 X13 from BF Goodrich.

In the anhydride-cured epoxy resins of the present invention, flexibility can also be achieved by increasing the spacing between the respective carboxyl groups of the anhydride. Linear anhydrides such as polysebasic polyanhydride (PSPA), polyazelaic polyanhydride (PAPA), and polyadipic polyanhydride (PADA), enhance the flexibility of the cured systems of the present invention and provide cross-linked epoxy resins with low cross-link densities. In contrast, ring stabilized anhydrides based on phthalic anhydride produce rigid systems due to the increased stabilization by the ring structure. As will be readily appreciated by those skilled in the art, chain substitution serves to decrease cross-link density and impart flexibility. Thus, for example, dodecenylsuccinic anhydride, will be observed to give a low heat distortion temperature, and therefore flexibility, due to its long side group.

Optional Additives

A component which can optionally and advantageously be included in the solder paste of the present invention is a surface tension reducing agent. It is used to reduce the contact angle of the solder paste and the bonding surfaces. The surface tension reducing agent may be a surfactant. Among the suitable surfactants are TWEEN®, available from ICI, Wilmington, Delaware, and potassium perfluoroalkyl sulfonates. When present, the surface tension reducing additive is preferably added in amounts of from about 0.1 weight % to about 1 weight % based on the weight of the organic component of the solder paste.

Another component that optionally is added to the solder paste composition of the present invention is an adhesion promoter which has the ability to enhance epoxy to metal bonding. Suitable adhesion promoters include organo silanes and titanates. A suitable organosilane is 6040, 3-glycidoxy-propyltrimethoxysilane available from Dow Corning Corp. of Midland, Michigan. A suitable titanate is LICA 38, neopentyl (diallyl)oxy, tri(diooctyl)pyro-phosphatotitinate available from Kenrich Petro Chemicals, Inc., in Bayonne, New Jersey.

The adhesion promoter is preferably added in amounts of from about 0.1 weight % to about 1% weight % based on the weight of the organic component of the solder paste.

Yet another component that can optionally be used in the encapsulating composition of the present invention is a defoaming agent such as FOAM BLAST™ 1326, an alkoxylate of fatty esters available from Ross Chemicals. The defoaming agent is preferably added in amounts of from about 0.1 weight % to about 1 weight % based on total weight of based on the weight of the organic component of the solder paste.

Solder Content

The solder powder of the solder paste of the present invention includes the broad spectrum of solder powders used in the solder pastes of the prior art. Suitably the solder powder content may fall within the range of about 65% by weight to about _95% by weight and preferably from about 85% by weight to about 92% by weight based on the total weight of the solder paste.

The following is an example of an epoxy-based solder paste that after use in reflow soldering leaves a probe-able, non-tacky residue.

EXAMPLE 7

The probe-able, non-tacky residue-forming composition is set forth below:

Component	Weight %
DGEBA resin (WPE 180-190)	3.5
Polyazelaic Polyanhydride	2.4
Stannous Octoate	0.1
Air Products Epodil L diluent	6.0
63 Sn/37 Pb-325 mesh solder powder	88.0

Solder powder accounts for 88% by weight of the formula while 12% is organic. This is a typical solder paste metal loading percentage. The organic component is an epoxy formulation that provides a low cross-link density when cured.

The organic polymer is composed of a solid polyanhydride which serves as a fluxing agent. They are solid at room temperature which helps provide the rheology to make a paste. The preferred polyanhydrides include polyazelaic

polyanhydride (PAPA), polyadipic polyanhydride (PADA), and polysebasic polyanhydride (PSPA).

This is blended with a liquid resin, a diglycidal ether of bisphenol A (DGEBA). Other resins, as can be appreciated by those skilled in the art, could be used including novolac resins, bisphenol F resins, etc. but it has been found that low cross-link densities are easily achieved with DGEBA resins, which are among the preferred epoxy resins.

The catalyst/accelerator, stannous octoate, provides latency to the cure of the epoxy/anhydride system. It is chosen specifically to allow soldering to take place in the reflow oven before significant gelation of the polymer.

A low molecular weight, liquid, aromatic hydrocarbon diluent, such as the Epodil L in the example, from Air Products, lowers the cross-link density of the cured product and dilutes the epoxy to allow the high metal loading level. The diluent in the formulation of Example 7 is the key to making the residue penetrable by a probe. Without the diluent the residue after reflow soldering is too hard to be penetrated by a probe. The diluent is not a solvent; it does not volatilize in the reflow oven. Other reactive (containing epoxy functional groups) or non-reactive diluents may be used to achieve the same effect.

The key to the probe-ability is to leave a flexible residue with a low cross-link density.

The choice of stannous octoate as an accelerator (cross-linking catalyst) prevents significant gelation of the epoxy during the ramp and soak stages to allow the soldering to take place when using a reflow temperature profile for Sn/37 Pb solder or alloys with similar melting points.

It is not intended to limit the solder paste or reflow soldering method of manufacture or solder paste binder selection and composition of the present invention to the particular embodiments described herein, and various modifications may be made, including, but not limited to, changes in the surface mount reflow profiles based on variations in the solder and hence solder melt temperature and conditions of solder melt, the dimensions, shape and materials, without departing from the scope and spirit of the

invention as set forth in the following claims.

I CLAIM:

1. A method of electrically connecting an electrical component having a plurality of metal bond site terminations to a component carrying substrate having a plurality of metal attachment sites corresponding to the terminations of said electrical component, at surface mount reflow profile conditions, as set forth in Fig. 1 utilizing a solder paste comprised of (1) a solder powder having a solder melt temperature with a particle size distribution of from about 20 to about 45 microns and present in an amount, based on total weight of the solder paste, of about 65% by weight to about 95% by weight; and (2) a binder comprised of a thermosetting resin and a cross-linking agent that acts, below the solder melt temperature, as a fluxing agent which removes oxide coatings from the surface of the metal bond sites on said electrical component and on said component carrying substrate and from the surface of said solder powder when heated to said solder melt temperature, said thermosetting resin and said cross-linking agent combination having a gel point at or above said solder melt temperature, which method comprises the steps of:

a) removing oxide coating from the surface of said metal bond sites and said solder powder while said binder is in liquid form;

b) melting the solder to electrically connect the electrical component having a plurality of metal bond site terminations to the component carrying substrate having a plurality of metal bond site terminations corresponding to the terminations of said electrical component while said binder is in liquid form and prior to said binder reaching its gel point; then

c) forming a binder gel; and then

d) curing said gel to form a binder residue encapsulating said electrical solder connections.

2. The method of Claim 1 wherein the amount by weight of solder powder, based on total weight of the solder paste, is above 85% by weight.

3. The method of Claim 1 wherein the thermosetting resin is an epoxide.

4. The method of Claim 2 wherein the thermosetting resin is an epoxide.

5. The method of claim 1 wherein the cross-linking agent is a polyanhydride or a carboxy terminated polyester.

6. The method of claim 2 wherein the cross-linking agent is a polyanhydride or a carboxy terminated polyester.

7. The method of claim 3 wherein the cross-linking agent is a polyanhydride or a carboxy terminated polyester.

8. The method of Claim 1, further comprising forming a flexible binder residue; then inserting a probe through said flexible binder residue into contact with said electrical connection to check the integrity of said connection; then, withdrawing said probe.

9. The method of Claim 3, further comprising forming a flexible binder residue; then inserting a probe through said flexible binder residue into contact with said electrical connection to check the integrity of said connection; then, withdrawing said probe.

10. The method of Claim 5, further comprising forming a flexible binder residue; then inserting a probe through said flexible binder residue into contact with said electrical connection to check the integrity of said connection; then, withdrawing said probe.

11. The method of Claim 7, further comprising forming a flexible binder residue; then inserting a probe through said flexible binder residue into contact with said electrical connection to check the integrity of said connection; then, withdrawing said probe.

12. A method of producing a low thermal mass assembly by electrically connecting an electrical component having a plurality of metal bond site terminations to a component carrying substrate having a plurality of metal attachment sites corresponding to the terminations of said electrical component utilizing a solder paste comprised of (1) a solder powder having a solder melt temperature and a particle size distribution of from about 20 to about 45 microns and present in an amount, based on total weight of the solder paste, of about 65% by weight to about 95% by weight; and (2) a binder comprised of a thermosetting resin and a cross-linking agent

that acts, below the solder melt temperature, as a fluxing agent which removes oxide coatings from the surface of the metal bond sites on said electrical component and on said component carrying substrate and from the surface of said solder powder when heated to said solder melt temperature, said thermosetting resin and said cross-linking agent combination having a gel point at or above said solder melt temperature, which method comprises ramping said low thermal mass assembly at the rate of about 1°C to about 4°C per second for a time sufficient to achieve solder melt and electrical interconnection and during said ramping effecting the steps of:

a) removing oxide coating from the surface of said metal bond sites and said solder powder while said binder is in liquid form;

b) melting the solder to electrically connect the electrical component having a plurality of metal bond site terminations to the component carrying substrate having a plurality of metal attachment site terminations corresponding to the terminations of said electrical component while said binder is in liquid form and prior to said binder reaching its gel point; then

c) forming a binder gel; and then

d) curing said gel to form a binder residue encapsulating said electrical solder connections.

13. The method of Claim 12 wherein the amount by weight of solder powder, based on total weight of the solder paste, is above 85% by weight.

14. The method of Claim 12 wherein the thermosetting resin is an epoxide.

15. The method of Claim 13 wherein the thermoset resin is an epoxide.

16. The method of claim 12 wherein the cross-linking agent is a polyanhydride or a carboxy terminated polyester.

17. The method of claim 13 wherein the cross-linking agent is a polyanhydride or a carboxy terminated polyester.

18. The method of claim 14 wherein the cross-linking agent is a polyanhydride or a carboxy terminated polyester.

19. The method of Claim 12, further comprising forming a

flexible solder residue; then inserting a probe through said flexible solder residue into contact with said electrical connection to check the integrity of said connection;

20. A solder paste for electrically connecting a metal bond site of a first electrical component to a metal bond site of a second electrical component and for forming a solder residue encased electrical solder connection between said first and second components at solder reflow conditions, comprising:

a) about 65% by weight to about 95% by weight based on total weight of solder paste of a solder powder having a solder melt temperature;

b) an epoxy resin;

c) a cross-linking agent for said resin that also acts as a fluxing agent that removes oxide coatings from the surface of said first and second electrical components and said solder powder below the solder melt temperature of said solder; and

d) a catalyst for catalyzing cross-linking of said epoxy resin with said cross-linking agent, the peak exotherm of said mixture of catalyst, epoxy resin, and cross-linking agent as measured using DSC at a ramp rate of 10° per minute being at or above the solder melting point whereby the gel point of said cross-linked epoxy resin is reached after solder melt.

21. The solder paste of claim 20, wherein the catalyst is tin octoate.

22. The solder of claim 21, wherein the cross-linking agent is a polyanhydride.

23. The solder paste of claim 20, further characterized in that, the solder residue is flexible, allowing a probe to pass through said solder residue and access the solder connection encased by said binder residue.

24. The solder paste of claim 23, further comprising a non-reactive flexibilizer which imparts flexibility to the solder residue after reflow soldering.

25. The solder paste of claim 23, further comprising a reactive flexibilizer that contains epoxy functional sites that, after reflow soldering, are incorporated into the

backbone of the cross-linked epoxy resin.

26. A method for selecting the components of binder component of a solder paste useful in forming encapsulated electrical interconnections in accordance with a surface mount reflow profile wherein the binder comprised of a thermosetting resin, a cross-linking agent that also acts as a flux and optionally a cross-linking catalyst which comprises:

a) identifying the melting point of the solder powder component;

b) heating the binder to a temperature exceeding the melting point of the solder;

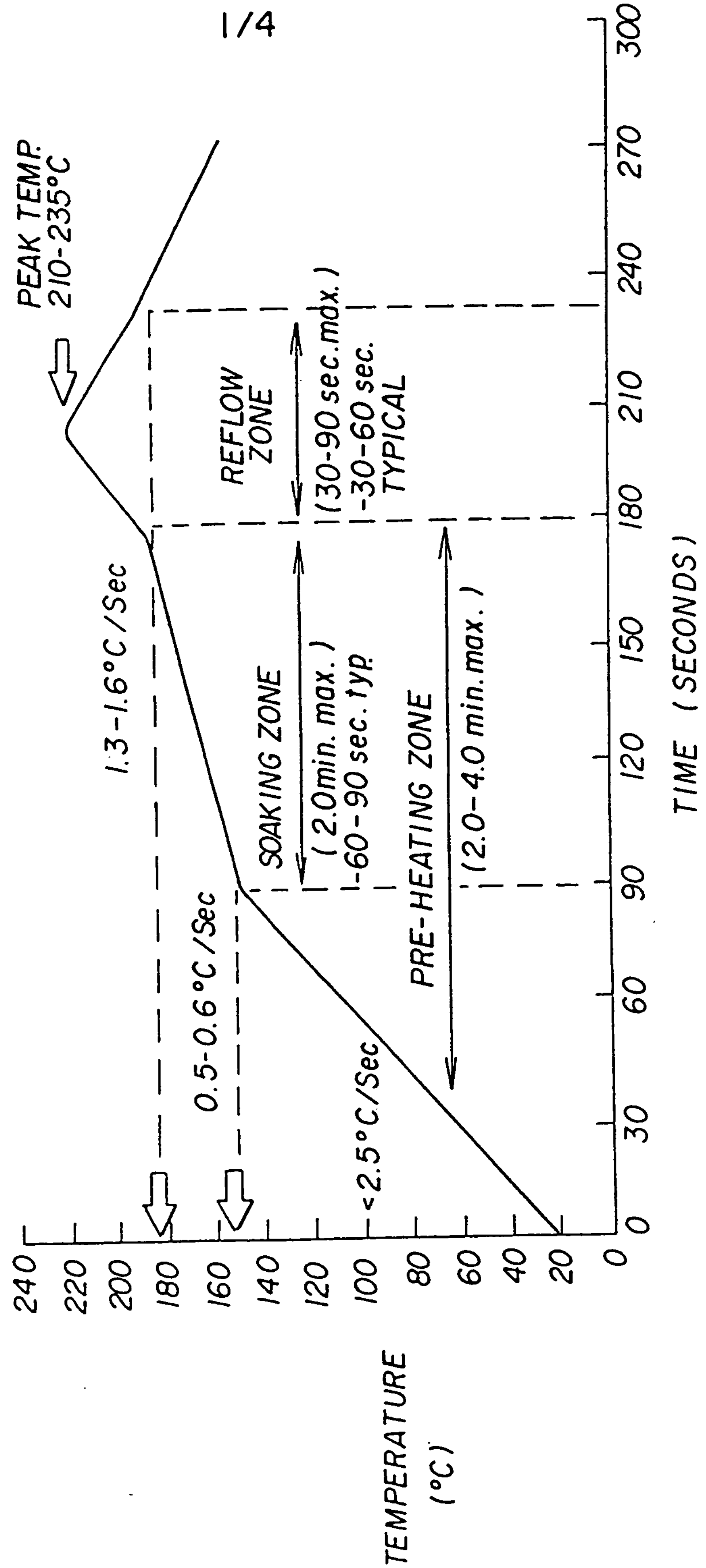
c) measuring the exothermic activity of the binder during heating step b); and,

d) identifying the temperature at which peak exothermic activity occurs; and

e) selecting as a binder for said solder paste a binder that displays peak exothermic activity at or above the melting point of the solder.

27. The method of claim 26, wherein the initiation of exothermic activity is identified and the criteria for binder selection also includes initiation of thermal reaction at a temperature that is no lower than 40°C below the solder melt temperature.

1/4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-30-60 sec. TYPICAL
1.3-1.6°C/Sec
SOAKING ZONE
(2.0min. max.)
-60-90 sec. typ
PRE-HEATING ZONE
(2.0-4.0 min. max.)
0.5-0.6°C/Sec
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TIME (SECONDS)
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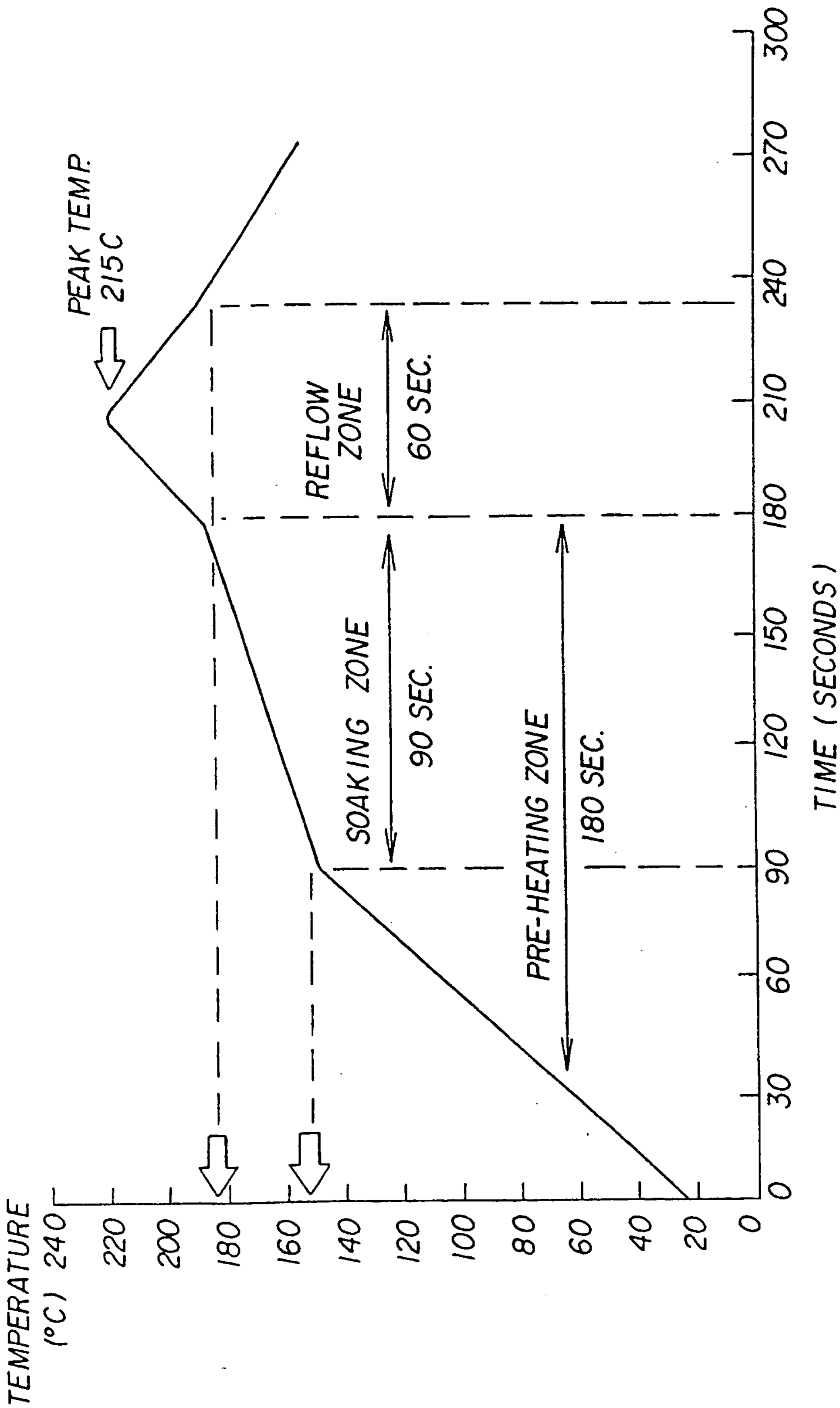
Fig. 1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(°C)
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220
200
180
160
140
120
100
80
60
40
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60
90
120
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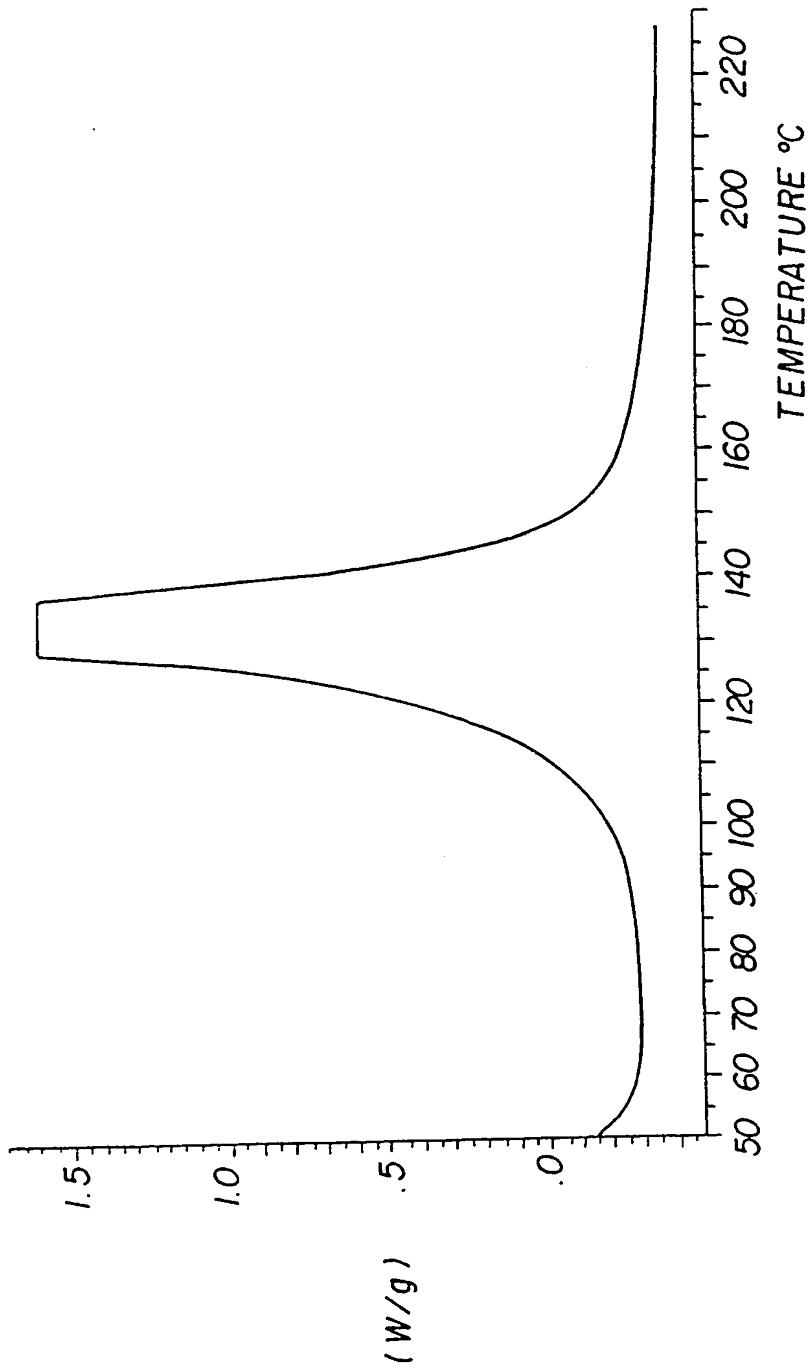
180
210
240
270
300
TIME (SECONDS)

Fig. 2



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140
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220
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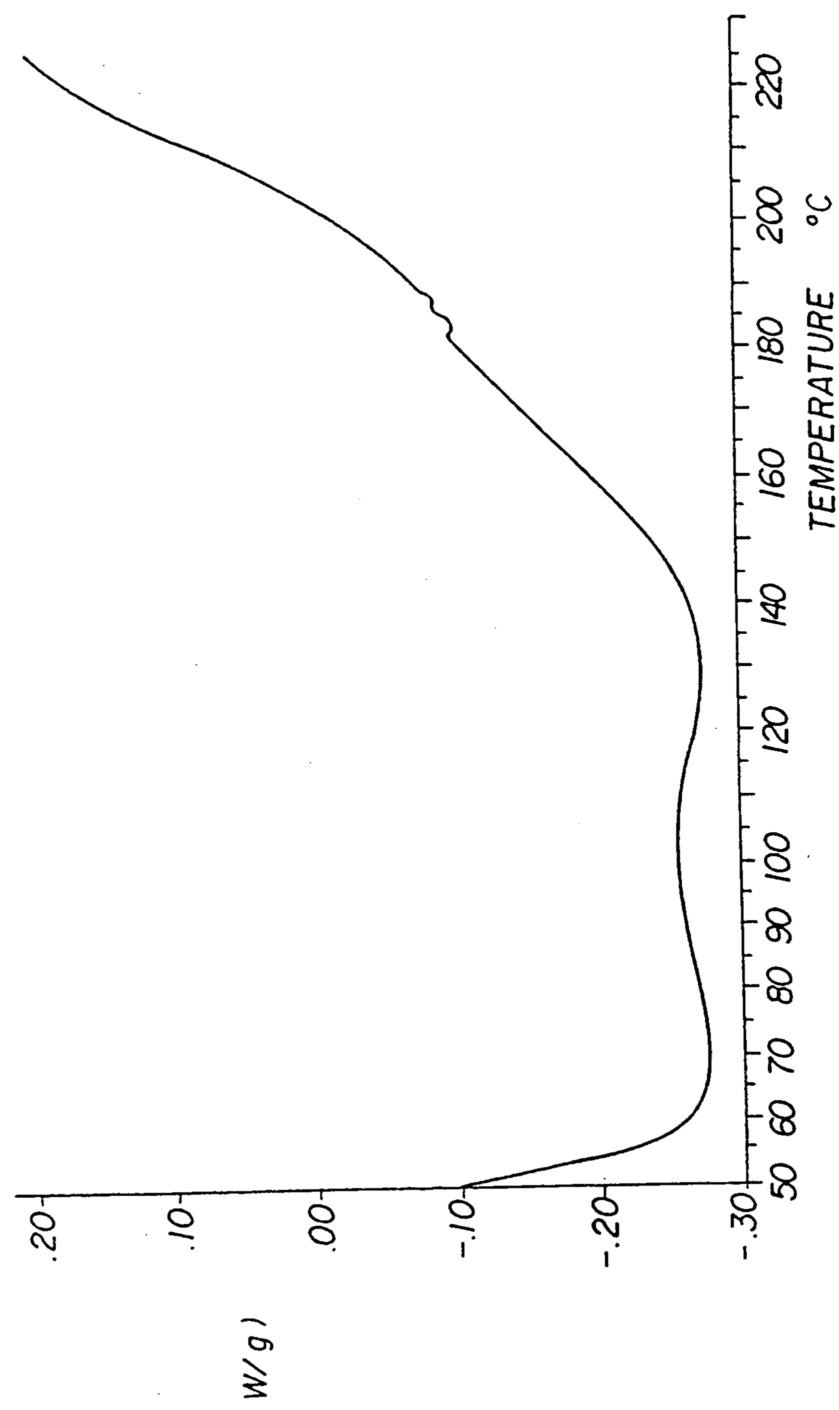
1.0
1.5
(W/g)

Fig. 3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(W/g)
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.00
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-.20
-.30

Fig. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/12761

A. CLASSIFICATION OF SUBJECT MATTER
IPC(6) :Please See Extra Sheet.
US CL :Please See Extra Sheet.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 257/778, 772; 228/233.2, 101; 528/92, 112; 525/438, 533; 252/512, 518; 428/413, 416, 418; 427/96

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,999,699 A (CHRISTIE ET AL) 12 March 1991, see entire document.	1-27
Y	US 5,376,403 A (CAPOTE ET AL) 27 December 1994, see entire document.	1-27

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
31 OCTOBER 1996	19 NOV 1996
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer MARGARET GLASS Telephone No. (703) 308-2351

Form PCT/ISA/210 (second sheet)(July 1992)★

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/12761

A. CLASSIFICATION OF SUBJECT MATTER:
IPC (6):

H01L 23/488; H01B 1/06; B05D 5/12; B32B 27/38, 15/08; C08G 59/68, 59/40

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

257/778, 772; 228/233.2, 101; 528/92, 112; 525/438, 533; 252/512, 518; 428/413, 416, 418; 427/96